

Proximate, Mineral and Antinutrient Compositions of Natural Cocoa Cake, Cocoa Liquor and Alkalized Cocoa Powders Sourced in Nigeria

Emmanuel Ilesanmi Adeyeye^{1*}

1. Department of Chemistry (Analytical Unit), Ekiti State University, PMB 5363, Ado-Ekiti, Nigeria.

Abstract

An investigation into the proximate, mineral and antinutritional constituents of natural cocoa powder (NCP), natural cocoa liquor (NCL) and alkalized cocoa powder (ACP) was carried out. Other parameters investigated were: energy values as contributed to the total metabolisable energy by protein, fat and carbohydrate and the energy percentages; calculated mineral quality parameters; mineral bioavailability as predicted by Ca: Phy, Phy:Zn and [Ca] [Phy]/[Zn] molar ratios of the different cocoa products and mineral safety index (MSI) of some of the minerals of the samples. The data generated were subjected to statistical evaluation of chi-square (χ^2). The three samples, NCP, NCL and ACP had proximate levels (g/100g) as: total ash, 3.73-10.8; moisture, 2.16-9.04; protein, 10.9-24.3; fat, 4.93-56.0; fibre, 1.03-17.3; carbohydrate, 20.5-48.9 and fatty acid, 3.95-44.8. For total energy contribution, results varied from, 1169-2656 kJ/100 g. In the minerals, the followings were highly concentrated: Na, K, Ca, Mg, Zn, Fe and P but low or not detected in Cu, Co and Mn. Virtually all the mineral quality parameters were poor as seen in these ratios: K/Na, Na/K, Ca/P and [K/(Ca + Mg)]. The molar ratios of the samples were good enough to predict the bioavailability of the minerals. The mineral safety index (MSI) values showed that no mineral reached the toxic level in any of the samples. In the antinutritional constituents, ACP was highest in phytin phosphorus (Pp), phytin and Pp % of P; NCL was highest in oxalate and total phosphorus (P); tannin was highest in NCP. χ^2 was significant in all proximate values (except ash, moisture and organic matter); all energy contributions, significant only in Mn (among the minerals); non was significant in the mineral quality parameters; only Ca: Phy was significant in the mineral molar ratios; no value was significant in the MSI and phytin was the only parameter significant among the antinutritional constituents.

Corresponding author:

Emmanuel Ilesanmi Adeyeye, Department of Chemistry (Analytical Unit), Ekiti State University, PMB 5363, Ado-Ekiti, Nigeria E-mail address: eiadeyeye@yahoo.com, adeyeyeilesanmi2012@gmail.com

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Introduction

Cacao was introduced into Nigeria from Fernando Po by Chief Squiss Ibanningo in 1874 at approximately the same time that Teteh Quashi introduced the crop into Ghana. The early development of the cacao industry in West Africa was entirely due to the initiative and entrepreneurship of the West African peasant farmers [1]. In Nigeria, the government has developed an interest in the cultivation of cacao since 1887 when cacao seedlings from the old Botanical garden at Ebute Metta (Lagos) were sent up-country (Ibadan) for trial. This explains why cacao cultivation gained its first and earliest impetus around Ibadan, Oyo State of Nigeria. In Ghana, Teteh Quashi planted the cacao seeds he introduced in a village west of Accra. The cultivation of cacao developed around the village and expanded through Koforidua, Tafo to the Ashanti region which is today the main cacao producing area of Ghana. In the Côte d'Ivoire, the first cacao plantings were at Bingerville, just outside Abidjan [2]. Nigeria is the world's fourth-largest producer of the cocoa beans. The mid – crop usually ends in June with the larger main crop starting in October.

While the majority of cocoa is exported as beans, first processing of other cocoa-derived products also takes place in Nigeria. Cocoa processing consists in the conversion of beans into cocoa butter and cocoa powder, two intermediary products and such conversion is operated by grinders (or converters). The quantity of butter obtained from the beans depends on the fat content of the beans, while powder is normally considered as a by-product of processing, as shells and paste. Butter and powder are subsequently recombined in different shares to obtain chocolate, with the addition mainly of milk and sugar. Cocoa powder is also used as a component in other confectionary products [3].

Exports of different cocoa products in Nigeria for year 2010 are as follows [4]:

- (i) Cocoa beans: 1,048,000,766 (exports, USD) and 588,438 (exports, tonnes).
- (ii) Cocoa shells: 38,739,754 (exports, USD) and 23,331 (exports, tonnes).
- (iii) Cocoa paste: 5, 427,083 (exports, USD) and 3,144 (exports, tonnes).
- (iv) Cocoa butter: 184,861,031 (exports, USD) and 16,118 (exports, tonnes).
- (v) Cocoa powder: 430,888 (exports, USD) and 60 (exports, tonnes).
- (vi) Chocolate: 5,548,053 (exports, USD) and 415 (exports, tonnes).

The type of cocoa grown in Nigeria is the Amelonado (melon shaped), a variety of Forastero [2].

Cocoa products are eaten mainly because they are liked, by young and old, owing to their attractive flavours and appearance which give pleasure in eating [5]. The nutritional parameters of cocoa are determined largely by the chemical composition of the material. The energy contribution to daily diets is dependent on the quantum of proteins, carbohydrates and fats in the cocoa products and its corresponding digestibility coefficient [5]. Cocoa powder is mainly used for low calorie food products. The minerals present in cocoa powder are important for their nutritional value. The level of fermentation, degree of alkalization, roasting and fat content determine the colour and flavour of cocoa products. Fermentation helps to generate proper aroma and reduces the level of acetic acid, which causes off-flavour in chocolate. The pH of cocoa liquors prepared from well fermented and dried West African beans is around 5.5 whilst those of unfermented or poorly fermented beans are 5.0 or less [6]. Cocoa is added to cigarettes for flavour enhancement. It also contains various psychoactive compounds, such as theobromine, caffeine, serotonin, histamine, tryptophan, tryptamine,

tyramine, phenylethylamine, octopamine and anadamide [7]. The levels of these compounds in added cocoa in cigarettes are thus critical to curtail possible addiction to cigarette smoking. Theobromine and theophylline, as well as caffeine, all found in this plant, are used as a diuretic, stimulant and also, in modern medicine, as an antiasthmatic [8].

Olaofe *et al.* [9] had reported on the metal contents of some cocoa beans produced in Ondo State, Nigeria and also reported on the quality assessment of some cocoa-based beverages in the Nigerian market. Adeyeye *et al.* [10] reported on the effect of farm and industrial processing on the amino acid profile of cocoa beans. Adeyeye and Ayejuyo [11] evaluated the proximate and mineral compositions of nibs and shells of processed ungerminated and germinated cocoa beans. There is, at present, scanty information on the nutritional composition profile of some industrially processed cocoa products on their relative concentrations. This study attempts to evaluate the proximate, mineral and antinutrient compositions of cocoa powder, alkalized cocoa powder and natural cocoa liquor from a major cocoa processing industry in Nigeria. This factory samples came from a blend of cocoa beans from different sources of similar species, which is the Forastero Amazonian Group.

Factory Processes

Basically the principle of processing cocoa beans into cocoa products has not changed in the past 150 years. Today, the beans are still cleaned, deshelled, roasted, and sometimes alkalized, then ground into cocoa liquor, which is subsequently pressed into butter and cake. Finally the cake is pulverized into powder. Cocoa processing developed during the 18th century in the Netherlands. In 1825, to reduce the fattiness of the chocolate drink, Coenraad Johannes van Houten developed a mechanical pressing process to fractionate the cocoa liquor, the result of grinding the roasted beans into a fatty fraction (cocoa butter) and a partially

defatted fraction (cocoa cake powder). Another process developed by van Houten was alkalization, or the "Dutch process," a procedure of treating cocoa with alkali. This was originally done in order to improve the solubility. It was found that at the same time, taste and colour were also changed [12]. The production flow sheet is as shown in Fig. 1 [12].

Roasting: The roasting process has the objective of reducing the water content and further developing flavour. Roasting is particularly important to the final flavour because the nib's flavour is formed from the precursors that develop during fermentation. Roasting temperatures range from 95-145 °C (200-295 °F) depending on the process, equipment, type of nib processed and the end product required.

After sterilization, the nib can be roasted directly (natural process) or can be alkalized first (Dutch process).

Alkalizing or Dutching: This consists of treating the cocoa nibs with an alkali solution such as potassium or sodium carbonate. It is practiced primarily to modify the colour and flavour of cocoa powder or cocoa liquor. Alkalization can be conducted at various points in the production process. Depending on the stage at which alkalization takes place, different results will be obtained. Nib alkalization is often preferred as it combines optimal flavour and colour development with minimal alkali usage.

Pressing: Cocoa butter constitutes about half the weight of the cocoa nib. This fat is partially removed from the cocoa liquor by means of hydraulic presses applying pressures as high as 450kg/cm². Depending upon the processing time and the setting of the press, the resulting cakes may have a fat content of 10-24%.

Materials and Methods

Procurement of Materials

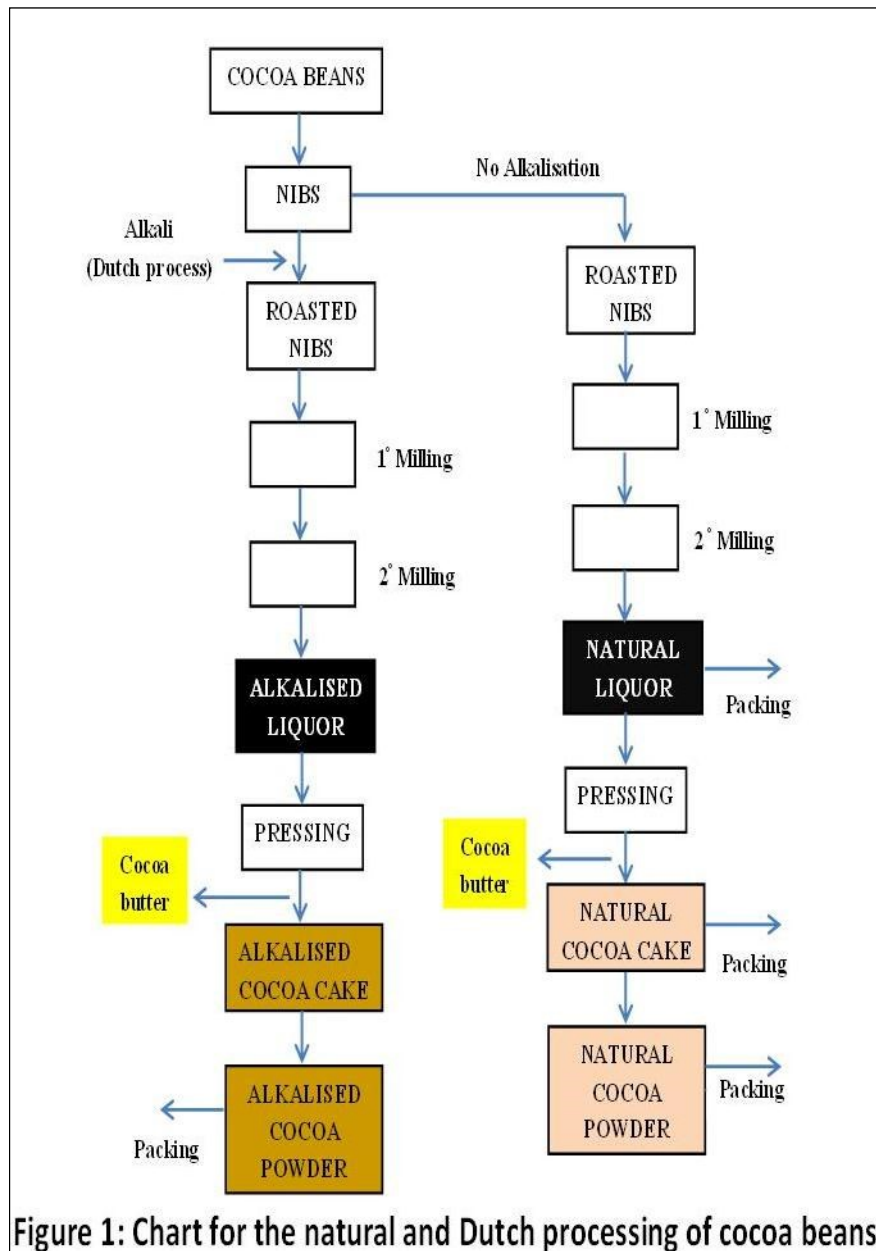


Figure 1: Chart for the natural and Dutch processing of cocoa beans.

Samples of the natural cocoa powder, alkalized cocoa powder and natural cocoa liquor were collected from the production line of Ile-Oluji Cocoa Products Ltd, Ile-Oluji, Ondo State, Nigeria in November 2011, for comparative analyses. The production process involved production of process line cocoa nibs (P-LCN) from cocoa beans.

The process-line cocoa nibs (P-LCN) was prepared from blended, cleaned and destoned dried cocoa beans from the factory's cleaner/destoner machine. The cocoa cake sample (CCS) was a product that resulted from further processing of the P-LCN. The processes involved microwave heating of the beans at a temperature range

of 90-100°C for a period of about 15 min on a vibratory bed (this made the cocoa bean shell puff for easy winnowing), automated roasting (at temperature range of 90-100 °C for about 20 min in a rotary evaporator), refining to over 98% fineness to obtain cocoa liquor (masse) which was further heat-treated at 80-90°C for about 12 h in storage tanks. The liquor was later fed in batches of about 200 kg sizes into a steam-jacketed vacuum mixer, where liquor homogenization and further heating took place for about 10 min before final pressing to obtain cocoa butter and cocoa cake. The final heating and homogenization were used to take the liquor from about 80 °C to about 105 °C and to ensure maturation of

the liquor. This also further ensured a final rapid evaporation of residual moisture to <1% in the cocoa liquor and guaranteed acceptable sterilization of the liquor. The pressed cake was kibbled mechanically to obtain smaller sizes of the cocoa cake solid, otherwise called pressed cocoa cake samples (PCCS). The factory samples were labeled natural cocoa powder (NCP), alkalized cocoa powder (ACP) and natural cocoa liquor (NCL) respectively. Figure 1 showed the natural and Dutch processing steps of cocoa beans. From these processes were obtained alkalized cocoa powder (ACP), natural cocoa powder (NCP) and natural cocoa liquor (NCL) samples for the various analyses.

Sample Treatment

The samples (ACP, NCP and NCL) were homogenized and ground to powder, using a Moulinex blender. The ground portions were kept in plastic bottles in the freezer (-4 °C) pending analysis. The values reported for each test were averages of two or more determinations.

Determination of Proximate Composition

Moisture content, total ash and crude fat were determined by the methods of the Association of Official Analytical Chemists (AOAC)[13]. Nitrogen was determined by the micro-Kjeldahl method, as described by [14] and the percentage nitrogen was converted to crude protein by multiplying by 6.25. The total carbohydrate was determined by difference. The calorific values in kilojoules (kJ) were calculated by multiplying the crude fat, protein and carbohydrate by Atwater factor of 37, 17 and 17 respectively. The crude fat values were used to calculate the total fatty acids by multiplying with a conversion factor of 0.80. The coefficients of variation percent were calculated [15].

Mineral Analysis

The minerals were analysed from the solution obtained by first dry ashing the samples at 550 °C. The filtered solutions were used to determine Na, K, Ca, Mg, Zn, Fe, Mn, Cu and Co by means of atomic absorption

spectrophotometer (Buck Scientific Model -200 A/210, Norwalk, Connecticut 06855) and phosphorus was determined colorimetrically by Spectronic 20 (Gallenkamp, UK) using the phosphovanado molybdate method [13]. All chemicals used were of British Drug House (BDH, London, UK) analytical grade. The detection limits for the metals in aqueous solution had been determined previously using the methods of Varian Techtron [16] giving the following values in µg/ml: Fe (0.01), Cu (0.002), Na (0.002), K (0.005), Ca (0.04), Mg (0.002), Zn (0.005), Mn (0.01) and Co (0.005). The optimal analytical range was 0.1-0.5 absorbance units with coefficients of variation from 0.9% to 2.21%.

The coefficients of variation percent were calculated [15]. Ca/P, Na/K, K/Na, Ca/Mg and the milliequivalent ratio $[K/(Ca + Mg)]$ [17]; the mineral safety index (MSI) [17] of Na, Mg, P, Ca, Fe and Zn were also calculated. The chi-square (χ^2) was compared with (χ^2_T) setting the level of confidence at $\alpha \leq 0.05$ [15].

The Phy/Zn, Ca/Phy and $[Ca] [Phy]/[Zn]$ molar ratios were also calculated [18].

Analysis of anti-nutrients

Tannin and Phytin: Finely milled samples (200 mg in 10 ml of 70 % aqueous acetone) were extracted for 2 h at 30 °C in water-bath using Gallenkamp orbital shaker (Surrey, UK) at 120 revolutions per min. Pigments and fat were first removed from the samples by extracting with diethyl ether containing 1% acetic acid. Thereafter, the total polyphenols (as tannic equivalent) was determined in 0.05 ml aliquot in test tubes by the addition of distilled water to make it to 1.0 ml, followed by the addition of 0.5 ml of Folin Ciocalteu reagent (Sigma) and then 2.5 ml of sodium carbonate solution. The tubes were vortexed and the absorbance recorded at 75 nm after 40 min as described by Makkar and Goodchild [19]. The amount of total polyphenols (as tannic equivalent) was calculated from the standard curve.

For the quantification of phytin, 8 g of each finely ground sample was soaked in 200 ml of 2 % hydrochloric acid and allowed standing for 3 h. The extract was thereafter filtered through two layers of hardened filter paper. Fifty milliliter of the filtrate was pipetted in duplicate into 400 ml capacity beakers before the addition of 10 ml 0.3 % ammonium thiocyanate solution as an indicator, and 107 ml of distilled water to obtain the proper acidity (pH 4.5). The solution was then titrated with a standard FeCl₃ solution containing 0.00195 g Fe/ml until a brownish yellow colour persisted for 5 min. Phytin-phosphorus (Pp) was determined and phytin (Phy) was calculated by multiplying the value of Pp by 3.5 [20]. Each milligramme of Fe is equivalent to 1.19 mg of Pp. Duplicate determinations of each sample were analysed.

Oxalate: 1g of the sample was weighed into 100 ml conical flask. Seventy five ml of 1.5 N H₂SO₄ was added and the solution was carefully stirred intermittently with a magnetic stirrer for about 1h and then filtered using Whatman no.1 filter paper. Twenty five milliliter sample extract (filtrate) was collected and titrated hot (80-90 °C) against 0.1N KMnO₄ solution to the point

when a faint pink colour appeared that persisted for at least 30 sec [21].

Other Calculated Parameters

The energy values as contributed by protein, fat and nitrogen-free extract of the samples were reported as follows: percentage proportion of total energy due to protein (PEP %), percentage proportion of total energy due to fat (PEF %), percentage proportion of total energy due to carbohydrate (PEC %) and percentage utilizable energy due to protein (UEDP %).

Results

The proximate data of the samples can be seen in Table 1. The total ash was highest in the ACP having value greater than the ash values of NCP and NCL put together; that is, ACP (10.8 g/100 g) but NCP (4.63 g/100 g) and NCL (3.73 g/100 g). The moisture was relatively low in the samples with value range of 2.16-9.04 g/100 g. The coefficient of variation percent (CV %) in the ash and moisture were relatively high but close with respective values of 60.0 and 58.9. The χ^2 values showed that no significant differences existed in the ash and moisture results as appropriate. The protein content was highest in the NCP, in fact, greater than the

Table 1. Proximate composition (g/100 g) of the cocoa products: natural cocoa powder (NCP), natural cocoa liquor (NCL) and alkalized cocoa powder (ACP)

Parameter ^a	NCP	NCL	ACP	Mean	SD ^b	CV % ^c	χ^2 ^d	Remark
Total ash	4.63	3.73	10.8	6.37	3.82	60.0	4.58	NS ^e
Moisture	6.56	2.16	9.04	5.92	3.48	58.9	4.10	NS
Protein (Nx6.25)	24.3	13.8	10.9	16.3	7.08	43.4	6.14	Significant
Crude fat	14.5	56.0	4.93	25.2	27.2	108	58.6	Significant
Crude fibre	1.03	3.80	17.3	7.37	8.70	118	20.6	Significant
Carbohydrate	48.9	20.5	47.1	38.9	15.9	40.9	13.0	Significant
Organic matter	95.4	96.3	89.3	93.6	3.82	4.08	0.312	NS
Fatty acid ^f	11.6	44.8	3.95	20.1	21.7	108	46.8	Significant
Energy (kJ/100 g)	1783	2656	1169	1869	747	40.0	598	Significant

^a Determinations were in duplicate. ^b SD = standard deviation. ^c CV % = coefficient of variation percent. ^d χ^2 = Chi-square calculated. ^e NS = value not significant at χ^2 Table value of 5.99 at degree of freedom (2) and confidence level of 0.05. ^f Crude fat x 0.80.

combined values in NCL and ACP. The crude fat in NCL was more than 50 % of the sample with a value of 56.0 g/100 g but very low in ACP with a value of 4.93 g/100 g. The crude fibre was very low in NCP (1.03 g/100 g) but relatively high in ACP (17.3 g/100 g). The following parameters had high concentration values: carbohydrate, organic matter (OM) and energy (kJ/100g). The following parameters had significant differences among themselves: protein, crude fat, crude fibre, carbohydrate, fatty acid and energy at $\alpha \leq 0.05$. All the CV % was high except in OM where it was 4.08.

The energy values as contributed to the total metabolisable energy by protein, fat and carbohydrate in the cocoa products samples were shown in Table 2. The fat, protein and carbohydrate values were each significantly different. All the energy values were each significantly different. All the energy values were high in each food part. The percentage energy values as contributed by protein, fat and carbohydrate in the

samples were shown in Table 3. The proportion of total energy due to protein (PEP) percent (PEP %) was highest in NCP, PEF % was highest in NCL and PEC % was highest in ACP. The total energy, PEP %, PEF % and PEC %, each had significant difference among themselves at $\alpha \leq 0.05$. The utilizable energy due to protein (UEDP) per cent (UEDP %) at 60 % utilization has this trend: NCP (13.9 %) > ACP (9.48 %) > NCL (5.29 %). UEDP % was also not significantly different at $\alpha \leq 0.05$.

The mineral composition (mg/100g) of the samples could be seen in Table 4. The following minerals were highly concentrated in the samples: Na (177-199), K (87.7-99.0), Ca (122-134), Mg (83.4-89.3), Zn (99.9-115), Fe (10.5-11.8) and P (696-736); Mn was low to high (1.18-12.0); Cu and Co were not detected in NCL. The statistical analysis showed that only χ^2 for Mn was significantly different in the mineral results. Most of the CV % values were much lower than those reported

Table 2. Energy values as contributed to the total metabolisable energy by protein, fat and carbohydrate in the cocoa products samples

Nutrient	NCP	NCL	ACP	Mean	SD	CV %	χ^2_c	Remark
Fat	537	2073	183	931	1005	108	2169	Significant
Protein	414	234	185	278	121	43.4	105	Significant
Carbohydrate	832	349	801	661	270	40.9	221	Significant

Determinations were in duplicate.

Table 3. Percentage energy values as contributed by protein, fat and carbohydrate in the cocoa products samples

Parameter ^a	NCP	NCL	ACP	Mean	SD	CV %	χ^2_c	Remark
Total energy	1783	2656	1169	1869	747	40	598	Significant
PEP %	23.2	8.81	15.8	15.9	7.2	45.2	6.51	Significant
PEF %	30.1	78	15.7	41.3	32.6	79	51.5	Significant
PEC %	46.7	13.1	68.5	42.8	27.9	65.2	36.4	Significant
UEDP %	13.9	5.29	9.48	9.56	4.31	45	3.88	NS

^aPEP = proportion of total energy due to protein, PEF = proportion of total energy due to fat, PEC = proportion of total energy due to carbohydrate, UEDP = utilisable energy due to protein, Determinations were in duplicate.

for the CV % values in the proximate composition. Some quality parameter ratios calculated from the mineral results were depicted in Table 5. All the CV % values were low at levels of 2.32-9.78. The following ratios were lower than the required quality standards: K/Na, Ca/Mg and [K/(Ca + Mg)] whereas Na/K ratios were higher than the required standards. No parameter ratio

promote Zn bioavailability. Among the molar ratio parameters, only the Ca x Phy had significant difference value at $\alpha \leq 0.05$. The mineral safety index (MSI) data were shown in Table 7. The following minerals had positive MSI: Na, Ca, Mg, Fe and P whereas negative MSI values were observed for Cu in NCP and for Zn in NCP, NCL and ACP. The CV % values were generally low

Table 7. Mineral safety index (MSI) of some of the minerals of the cocoa products samples

Mineral	Mineral safety index			Mean	SD	CV %	χ^2_c	Remark
	NCP	NCL	ACP					
Na	1.70	1.75	1.92	1.79	0.113	6.31	0.014	NS
Ca	1.02	1.12	1.09	1.08	0.05	4.83	0.005	NS
Mg	3.13	3.29	3.35	3.26	0.116	3.56	0.061	NS
Zn	220	252	234	235	16.4	6.97	2.29	NS
Cu	43.6	ND	25.0	34.3*	13.1*	38.4*	5.04*	NS
Fe	5.26	5.37	4.67	5.10	0.374	7.34	0.055	NS
P	5.80	6.14	6.05	6.00	0.177	2.95	0.010	NS

*Values based on the results from NCP and ACP.

Determinations were in duplicate.

was statistically significant at $\alpha \leq 0.05$. Also the Ca:Phy, Phy:Zn and $[Ca][Phy]/[Zn]$ concentrations were shown in Table 6. Ca:Phy molar ratio was higher than the critical level of 6:1, this meant that Zn bioavailability would not be impaired under this model. Also, all the samples showed Phy:Zn levels less than 1.0 meaning that the samples Zn would be bioavailable under this model. From the results in Table 6, all the Ca x Phy:Zn values were lower than 0.5 mol/kg and therefore would

and all were not significantly different at $\alpha \leq 0.05$.

The antinutrient constituents were shown in Table 8. The phytin was moderately high at 48.2 – 88.7 mg/100g but the phytin phosphorus (Pp) was low at 13.6-18.8mg/100g (or Pp % of P at 1.84-3.44). Both tannin and oxalate were also low. The CV % values ranged from 2.95-42.0 with phytin showing significance difference at $\alpha \leq 0.05$ among the parameters.

Discussion

Table 8. Antinutritional constituents of the cocoa products samples (mg/100 g)

Constituent	NCP	NCL	ACP	Mean	SD	CV%	χ^2_c	Remark
Pp ^a	17.9	13.6	25.0	18.8	5.77	30.7	3.54	NS
Phytin	63.4	48.2	88.7	66.8	20.5	30.7	12.6	Significant
Oxalate	2.48	6.03	4.19	4.23	1.78	42.0	1.49	NS
Tannin (g/100g)	8.72	4.72	5.35	6.26	2.15	34.4	4.30	NS
Total phosphorus	696	736	726	720	21.2	2.95	1.26	NS
Pp % of P	2.57	1.84	3.44	2.62	0.80	30.6	0.488	NS

^aPhytin phosphorus.

Determinations were in duplicate.

The proximate composition in Table 1 showed that moisture content ranged from 2.16-9.04 g/100 g. Cocoa powder is hygroscopic. If a cocoa powder has an excessive level of moisture, flavour may deteriorate. Because cocoa powder is hygroscopic, good packaging and storage conditions are essential to preventing the take-up of moisture. Cocoa powder is safe at a moisture content of up to 5 % [12]. The NCP in this report was 6.56 g/100 g which was close to 5.0 %.

The natural ash content of non-alkalized cocoa powder is approximately 6.0 % of the fat-free dry material [12]. In the present results, total ash was 4.63 g/100 g (NCP), 3.73 g/100 g (NCL) and 10.8 g/100 g (ACP). The ash content in ACP could be affected by the type and quantity of alkalis used in the alkalization process itself. The EU directive 95/2/EC on food additives other than colours and sweeteners allows max. 7 % K_2CO_3 (or equivalent on fat-free dry basis) to be added for alkalization [12].

Most commercially available cocoa powders contain between 10 and 24 % fat while the 10-12 % fat range is the most frequently used. The crude fat in the samples was 14.5 g/100 g (NCP) and 4.93 g/100 g (ACP) whereas the crude fat in the NCL was greater than 50 % fat having a value of 56.0 g/100 g. The protein content of the samples was widely varied with the NCP value (24.3 g/100 g) being about two times the value in NCL (13.8 g/100 g) and 2½ times the value in ACP (10.9 g/100 g). A value of 23 g/100 g was recorded in literature for non-alkalized cocoa powder [12].

The dietary fiber in the samples ranged as follows: NCP (1.03 g/100 g) < NCL (3.80 g/100 g) < ACP (17.3 g/100g). These values were all less than the value reported in literature as 32 g/100 g each for non-alkalized, lightly alkalinized and strongly alkalinized [12]. This high difference could be due to the different sources of the cocoa beans since similar methods of determination were used for the analyses. Dietary fibre in cocoa products is the collective term for the structural

parts of plant tissues that are not or only partly digested. It is the modern term for what used to be referred to as "roughage" or "bulk". In recent decades, it has been established that a diet high in fiber is recommended. Dietary fiber has been found to reduce the risk of cancer in the digestive tract. The indigestible cellulose in the fiber may absorb water and provide roughage for better functioning of the alimentary system [22].

The energy content ranged from 1.169-2.656 MJ (mega Joule) showing them to be good sources of concentrated energy, this was due to their high protein, carbohydrate and fat content levels. Energy from cereals range from 1.3-1.6 MJ/100 g [23]; it was 2.55-2.71 MJ/100 g in various treated groundnut seed flours [24]; both were favourably comparable to the present results. The energy from the proximate results in turkey-hen ranged from 1.33-1.37 MJ/100 g [25] which were also close to the value of ACP in the present results.

The organic content range of 89.3-96.3 g/100 g had high correlation with the values reported for various treated groundnut seed flours having range values of 96.5-97.6 g/100 g [24]. The present results OM were in contrast to animal OM where the muscle and skin were almost 100 per cent OM, like in turkey-hen where OM in muscle was 99.3 g/100 g and skin OM was 99.2 g/100 g [25]. The calculated total fatty acids in the samples had values of 11.6 g/100 g (NCP), 44.8 g/100 g (NCL) and 3.95 g/100 g (ACP). The value of 3.95 g/100 g in ACP was much lower than in the other two samples; this could be due to the fact that some of the dietary oil had been saponified during alkalization process in the preparation of ACP. The calculated fatty acids in various treated groundnut seed flours ranged from 43.0-47.3 g/100 g [24] whose values were close to the value of NCL. It had been shown that about 60 % of the fatty acids present in cocoa butter (stearic and palmitic) are characterized as saturated fatty acids, a number of clinical research studies suggest cocoa butter, and

stearic acid in particular, do not function the same as other saturated fats in vivo. Stearic acid consumption has not led to increasing levels of blood cholesterol and therefore is characterized as having a neutral effect [12, 26].

The total energy from fat, protein and carbohydrate as contributed by NCP, NCL and ACP could be seen in Table 2. Contributions of fat and protein to total energy in ACP were low but high in carbohydrate. NCP fat and protein contributed to the total energy moderately but carbohydrate contribution was high. In NCL, energy contributions from protein and carbohydrate were moderate but very high contribution from fat. Interest in the calorific value of food products is currently high because of consumer's sensitivity to diet. The amount of cocoa powder in a product is generally low in comparison to, for example, sugars and fats. The caloric value of cocoa powder is also intrinsically low [12]. Cocoa powder thus contributes little to a product's total caloric value and thus has minimal effects on total energy intake.

The daily energy requirement for an adult is between 10455-12548 kJ depending on his physiological state whilst that of infants is 3095kJ [27]. This implies that while an adult man would require between 394-894 g cocoa sample (lower energy requirement) to meet his minimum requirement, an infant would require 117-265 g depending on whether this calculation came from NCP, NCL and ACP. All these calculations could be depicted from Table 3. The utilizable energy due to protein (UEDP %) for the samples (assuming 60 % utilization) was 13.9 (NCP), 5.29 (NCL) and 9.48 (ACP). The UEDP % values from NCP and ACP were each greater than the recommended safe level of 8 % for an adult man who requires about 55 g protein per day with 60 % utilization. This showed that the protein concentration in the NCP and ACP samples would be more than enough to prevent energy malnutrition particularly in adults fed solely on NCP and ACP as the main source of protein.

The PEF % (Table 3) was low in ACP (15.7 %) which was lower than the recommended level of 30 % [28] and 35 % [29] for total fat energy intake, this is useful for people wishing to adopt the guidelines for a healthy diet. PEF % in NCP (30.1) fell within the two standard range whereas NCL PEF % of 78.0 was far away from the standard.

The minerals shown in Table 4 were those for which the greatest interest exists. The natural potassium content of cocoa powder is relatively high at approximately 2 %; in this report, the range of potassium was 87.7-99.0 mg/100 g (Table 4). As a result of alkalization with potassium carbonate, this number may rise to 5 % [12]. Whilst the potassium was 99.0 mg/100 g (NCP), it was 95.5 mg/100 g (ACP) in the present results, showing that the alkalization might not be due to the use of K_2CO_3 . In the manufacture of dark brown powders, sodium hydroxide is often used. This can raise the natural sodium content of 0.01% to more than 2 %. In these results, the sodium ranged from 177-199mg /100g (or 0.177-0.199 %) showing that the alkalization process might have involved the use of a sodium compound. Cu and Co were not detected in NCL. The non-detection of both Cu and Co in NCL could be that the two minerals were resident in the cocoa butter which only formed 56 % of the NCL. ACP was highest in concentration in Na, Mg and Ca; NCL was highest in Ca, Zn, Mn, Fe and P meaning NCL was a major source of most of the trace minerals and infact most of the minerals; NCP was highest in K and Cu on pairwise comparison. The P levels of 696-736 mg/100 g was close to 800 mg recommended daily allowance (RDA) where Ca levels of 122-134 mg/100 g was much below the RDA level of 800 mg. Na and K levels were both lower than the RDA levels [30], these values might lead to dietary stress if depended upon as the sole source of Na and K. The lower level of K than Na disagreed with what was observed in vegetable materials [31]. The Ca levels were about double the Mg levels; in groundnut seed flours,

the Mg level was about double the Ca level (except in the cooked sample) [24]. The Fe values were relatively high at 10.5-12.0 mg/100 g. The daily Fe requirement by humans are 10-15 mg for children, 18 mg for women and 12 mg for men and it is present in the enzyme cytochrome oxidase involved in energy metabolism [32]. Calcium behaves as a kind of co-ordinator among inorganic elements; if excessive amounts of K, Mg or Na are present in the body, Ca is capable of assuming a corrective role. If the amount of Ca is adequate in the diet, Fe is utilized to better advantage. This is an instance of 'sparing action' [32]. The Zn levels were 99.9-115 mg/100 g which is above the Zn allowances of about 15-20 mg per day [32]. Mn activates enzymes involved in the transfer of phosphate and hydroxyl groups as well as some hydrogenation reactions [33]. The values of Co ranged from ND-1.97 mg/100 g. Co (II) is a component of vitamin B₁₂ (cyanocobalamin) which is essential for the prevention of anaemia, also Cu values ranged from ND-3.96 mg/100 g, this mineral plays important roles in enzymes activities [34]. Mn was high here unlike what it obtains in animal sources [35].

The mineral concentration ratios were shown in Table 5. The K/Na range was 0.48-0.56. These values were low. K/Na enhances the salt balance of the body fluid; for this K/Na should be a minimum of 1.0. Also the Na/K ratios were 1.79-2.09; all these values were greater than 0.60 to avoid high blood pressure [36]. The Ca/P ratios of 0.18 (all values) were very low, the ratio results could be described as being poor; for this reason, one should be careful for such food unless food is good for other reasons. The Ca/Mg ratios were 1.47-1.53; these values were much greater than the recommended value of 1.0 [30]. The Ca/P ratio is reported to have some effect on Ca in blood of many animals [30]. The [K/(Ca+Mg)] obtained was 0.79-0.96 milliequivalent. To prevent hypomagnesemia, [37] reported that the milliequivalent of [K/(Ca+Mg)] must be less than 2.2, this was the case

in this report. This was due to low K but high Ca + Mg levels.

The Phy: Zn, Ca:Phy and Ca x Phy: Zn molar ratios were depicted in Table 6. Oberleas and Harland [38] showed that foods with a molar ratio of Phy: Zn less than 10 showed adequate availability of Zn and problems were encountered when the value was greater than 15. In the present study all the samples showed Phy:Zn levels of less than 1.0 meaning that the samples Zn would be bioavailable under this model. In human studies, Phy:Zn molar ratios of 15:1 had been associated with reduced bioavailability [39]. Wise [40] suggested that the solubility of phytates and the proportion of Zn bound in a mineral complex in the intestines depends on the levels of Ca. In his model, Phy precipitation is not complete until dietary Ca: Phy molar ratios attain a value of approximately 6:1. At Ca:Phy molar ratios lower than 6:1, Phy precipitation is incomplete, so that some of the dietary Zn remains in solution. The proportion remaining in solution increases with decreasing Ca:Phy molar ratios [40]. In the present study no Ca:Phy molar ratio was lower than this critical level of 6:1, this meant Zn bioavailability would also not be impaired under this model. Ferguson *et al.* [41] showed that the molar ratio varies with different foods and recommended that this value be used in conjunction with other data to explain the availability of Zn using the Ca:Phy ratio. Ellis *et al.* [42] and Davies and Warrington [43] indicated that the ratio of Ca x Phy: Zn is a better predictor of Zn availability and noted that if the value is greater than 0.5 mol/kg, then there would be interference with the availability of Zn. From the results in Table 6, all the Ca x Phy: Zn values were lower than 0.5 mol/kg and therefore would promote Zn bioavailability. The Ca x Phy: Zn results were in agreement with the report of Adeyeye *et al.* [44] in 35 foods of major consumption in Nigeria but much better than the results obtained for 13 Nigerian spices [45] and in seven varieties of Nigerian garden egg fruits [46]; present results were also in

Table 4. Mineral composition (mg/100 g) of cocoa products samples

Component	NCP	NCL	ACP	Mean	SD	CV %	χ^2c	Remark
Na	177	183	199	186	11.7	6.31	1.48	NS
K	99	87.7	95.5	94.1	5.79	6.16	0.718	NS
Ca	122	134	131	129	6.23	4.83	0.604	NS
Mg	83.4	87.8	89.3	86.8	3.09	5.56	0.22	NS
Zn	99.9	115	106	107	7.45	6.97	1.04	NS
Cu	3.96	ND ^a	2.27	- ^b	-	-	-	-
Co	1.06	ND	1.97	-	-	-	-	-
Mn	1.93	12	1.18	5.04	6.05	120	14.5	Significant
Fe	11.8	12	10.5	11.4	0.84	7.34	0.119	NS
P	696	736	726	720	21.2	2.95	1.26	NS

^aND = not detected. ^bNot applicable.

Determinations were in duplicate.

Table 5. Some quality parameters calculated from the mineral results

Parameter	NCP	NCL	ACP	Mean	SD	CV %	χ^2c	Remark
K/Na	0.56	0.48	0.48	0.51	0.05	9.06	0.008	NS
Na/K	1.79	2.08	2.09	1.99	0.17	8.56	0.029	NS
Ca/P	0.18	0.18	0.18	0.18	-	-	-	-
Ca/Mg	1.47	1.53	1.47	1.49	0.03	2.32	0.002	NS
[K/Ca + Mg] ^a	0.96	0.79	0.87	0.87	0.09	9.78	0.017	NS

^aMilliequivalent.

Determinations were in duplicate.

Table 6. Ca: Phy, Phy: Zn and [Ca][Phy]/[Zn] molar ratios of the different cocoa products samples

Parameter	NCP	NCL	ACP	Mean	SD	CV %	χ^2c	Remark
Ca: Phy ^a	31.8	45.9	24.4	38.9	9.97	25.7	7.91	Significant
Phy:Zn ^b	0.063	0.042	0.082	0.062	0.02	32.3	0.013	NS
[Ca][Phy]/[Ca] ^c	0.002	0.001	0.003	0.002	0.001	50	0.001	NS

^amg of Ca/MW (molecular weight) of Ca:mg of Phy/MW of Phy.

^bmg of Phy/MW of Phy:mg of Zn/MW of Zn.

^c[mol/kgCa]x[mol/kgPhy]/[mol/kgZn].

Determinations were in duplicate.

perfect agreement with the report of Adeyeye [24] in groundnut seed flours and in seven mushrooms consumed in Nigeria [47].

The mineral safety index (MSI) (as shown in Table 7) had these standards for the minerals determined: Na (4.8), Ca(10), Mg(15), Zn (33), Cu(33), Fe(6.7), P(10) [17]. In all the samples, each of the Zn MSI was greater than 33 by 187 (NCP), by 219 (NCL) and by 201(ACP); and in Cu it was greater than 33 by 10.6(NCP). Other calculated MSI levels were lower than the maximum MSI. Since all the Zn MSI values were greater than 33, this meant all the samples have Zn values far above the recommended adult intake. The minimum toxic dose is 500 mg, or 33 times the RDA [17]. Zn supplements can decrease the amount of high density lipoprotein (HDL) circulating in the blood, increasing the risk of heart disease [48]. In animals, Zn supplements decrease the absorption of Fe so much that anaemia is produced [49]. Intakes of Zn only 3.5 mg/day above RDA decrease Cu absorption [50]. In animals, Cu deficiency causes scarring of the heart muscle tissue and low levels of Ca in bone [48]. From the foregoing, all the samples would lead to excess Zn consumption with its deleterious effects. Other samples from literature that can cause the deleterious effect of Zn absorption in the small intestine due to very high MSI [51] were: scales of cobra and scales of wart (both snakes), scales of both sole and silver fish and some fast foods [52].

The anti-nutritional factors were depicted in Table 8. The trends shown were: ACP was highest in Pp, phytin and Pp% of P; NCL was highest in oxalate and total phosphorus whereas NCP was highest only in tannin. The phytin (Phy) levels were lower than many literature values such as 13 spices (390-6210 mg/100 g) obtained in Nigeria [45]; seven varieties of Nigerian garden egg fruits (507-2788 mg/100 g) [46]; many other Nigerian foods such as legumes (14-344 mg/100 g), cereals (112-287 mg/100 g), spices (35-184 mg/100 g) and tubers/ roots (0.0-1070 mg/100 g) [44]. In differently processed

Canavalia ensiformis and *Mucuna pruriens* seed flours, Phy range was 5.1-18.5mg/100g and 6.0-15.3mg/100g respectively [53]. In 17 wild leguminous crop seeds, values of Phy ranged from 0.23-1.03g/100 g [54] which was much higher than in the cocoa products samples. The present results also had Phy levels lower than the report of Oke [55], Harland *et al.* [56] and Harland and Oberleas [57] in raw beans, raw and fermented corn products, raw fruits and vegetables, raw and fermented tubers. Phytin values in processed groundnut ranged from 33.4 -37.8 mg/100 g [24] which were lower than the present results.

The Pp in the present study was much lower than in the 17 wild leguminous crop seeds with values of 0.06-0.29g/100g [54] compared with the present study of 13.6-25.0 mg/100 g. But the present Pp values were higher than in *C. ensiformis* (1.4-5.44 mg/100 g) and *M. pruriens* (1.7-4.3 mg/100 g) [53]. The Pp % of P range of 1.84-3.44 was close to the value of 2.28-2.67 in groundnut seed flours [24], but lower than in the 17 wild leguminous crop seeds of 11.4-84.1 [54] which showed that the P of the present study were only linked to Pp to the tune of 1.84-3.44 which would not affect the utilization of divalent minerals and also will not render unavailable some essential amino acids. Also monogastric animals will have no problem in utilizing the cocoa products.

The observation about the tannin content in the samples tended to suggest that the processing techniques adopted had reasonable effects on its values. The tannin range was 4.72-8.72 g/100 g. During fermentation, roasting and alkalization of the cocoa, mono-and oligomeric-catechins may be partially polymerized into tannins. Tannins play an important role in colour formation and partly influence flavour. In addition, with the increase of molecular weight, reactivity with proteins and peptides increases. As a result, complexes that reduce the digestibility of protein are created. Tannin is known to possess antioxidative properties in vitro as well

as certain potential preventive effects against a number of chronic conditions including cancer and cardiovascular disease.

The oxalate ranged from 2.48-6.03 mg/100 g. This was close to the values in groundnut seed flours with value range of 4.08-6.42 mg/100 g [24]. The presence of oxalate has an undesirable effect on Ca absorption and utilization. This acid combines with Ca to form a compound known as calcium oxalate, which passes through the intestine without being absorbed. The amount of oxalate formed will depend on the amount of oxalic acid in the food [32]. About half of all kidney stones are calcium oxalate, either alone or mixed with the salts of calcium phosphate, magnesium ammonium phosphate and calcium carbonate. Formation of these stones frequently reflects chronic alkalinity of bladder and renal pelvic urine caused by infection with bacteria that hydrolyse urea, releasing ammonia [58]. This study showed that special treated samples like alkalization and formation of liquor enhanced the oxalate level twice in ACP and trice in NCL when compared with the NCP.

Conclusion

Alkalization of cocoa powder enhanced the levels of total ash, moisture and crude fibre; cocoa liquor formation enhanced crude fat, organic matter and energy; whereas natural cocoa powder was best in crude protein and carbohydrate. The contribution of fat to total energy was moderate in NCP and ACP; ACP and NCP contributions to utilizable energy due to protein were above average. Zinc was too much concentrated in all the samples and might lead to some deleterious effects. More potassium would be required to balance the K/Na and Na/K ratios, also same to Ca in Ca/P ratios. The oxalate levels could cause anxiety because of the formation of kidney stones. On the whole, the samples met a very high level of positive nutritional recommendations.

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